

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representation of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

New Zealand No. 276069

International No. PCT/EP94/03589

**TO BE ENTERED AFTER
ACCEPTANCE AND PUBLICATION**

Priority dates: 08.11.1993;

Complete Specification Filed: 28.10.1994

Classification: (6) B32B27/32; B65D65/40

Publication date: 19 December 1997

Journal No.: 1423

NEW ZEALAND

PATENTS ACT 1953

COMPLETE SPECIFICATION

Title of Invention:

Multilayered, bioriented, heat shrinkable film

**Name, address and nationality of
applicant(s) as in international
application form:**

**W.R. GRACE & CO. - CONN., COMPANY of 100 Rogers Bridge Road, Duncan,
SC29334-0464, United States of America**

MULTILAYERED, BIORIENTED, HEAT SHRINKABLE FILM

5

FIELD OF THE INVENTION

The present invention relates to a multilayer, bioriented, heat shrinkable film, a method for the manufacture thereof and use thereof for packaging food products and consumer articles.

More particularly, the present invention relates to a
10 multilayer, bioriented, heat shrinkable film extruded from a flat die and stretched both in machine direction and in cross-direction wherein at least one layer comprises at least one ethylene/alpha-olefin C_4-C_{12} copolymer.

BACKGROUND OF THE INVENTION

15 Multilayer heat shrinkable films have been known for a long time.

U.S. patent 4,532,189 (W.R. Grace & Co.) discloses a multilayer, heat shrinkable film comprising:

- (A) a core (central) layer comprising a linear low density
20 polyethylene or a linear medium density polyethylene;
(B) two skin (external) layers comprising a blend of from 70% to 90%, by weight, of an ethylene/propylene copolymer and from 10% to 30%, by weight, of a propylene homopolymer;
wherein said film has an average machine direction free shrink
25 at 200°F of at least 12% and an average cross-direction free shrink at 200°F of at least 17%.

The core layer may also comprise other polymers such as, for example, ethylene/propylene copolymers, ethylene/vinyl acetate copolymers, ionomer resins and non-linear low density poly
30 ethylenes.

- 2 -

Moreover, said film may also comprise two intermediate layers comprising a blend of approximately 90% by weight of an ethylene/vinyl acetate copolymer and approximately 10% of an ionomer resin.

5 U.S. patent 4,551,380 (W.R. Grace & Co.) discloses a multilayer heat shrinkable film comprising:

- (A) a cross-linked core layer consisting essentially of a linear low density polyethylene; and
- (B) two surface layers comprising essentially a blend of (1) a
10 linear low density polyethylene, (2) a linear medium density polyethylene and (3) an ethylene/vinyl acetate copolymer.

GB-A-2,097,324 discloses heat shrinkable films manufactured by stretching, at least three times their original linear
15 dimension in at least one direction, a film having the following homogeneous composition:

- (A) 5-100%, by weight, of at least one linear copolymer of ethylene with at least one C_8-C_{18} alpha-olefin, said copolymer having the following characteristics:
 - 20 (a) melt index of 0.1-4.0 g/10 min.;
 - (b) density of 0.900-0.940 g/cm³;
 - (c) stress exponent above 1.3; and
 - (d) two distinct crystallite melting regions below 128°C as determined by differential scanning calorimetry (DSC),
25 the temperature difference between said regions being at least 15°C; and
- (B) 0-95%, by weight, of at least one polymer selected from the group consisting of ethylene homopolymers and copolymers of ethylene with an ethylenically unsaturated comonomers, said
30 polymer having only one crystallite melting point below

- 3 -

128°C;

with the proviso that stretching is carried out within the temperature range defined by the two melting points of the crystallites of the etnylene/alpha-olefin copolymer of the above paragraph (A).

These films are manufactured by the well-known air bubble technique. An example of method and equipment of this technique is disclosed by U.S. patent 4,841,605.

However, the films obtained with this technique have the disadvantage of not having sufficiently uniform thickness and planarity. In fact the total thickness variation in said films is $\pm 15\%$ while, as regards planarity, it has defects consisting of deviations from a straight line (snaking) and sags. More particularly the average deviations from a straight line (snaking) is approximately 50 mm, whereas the average sag is approximately 35 mm.

In addition to the air bubble technique, stretching the films also by the so-called "tenter frame" technique is known. Examples of machines suitable for implementing this technique are disclosed by U.S. patents 3,148,409 and 3,201,826.

The tenter frame technique, also known as "flat orientation technology", consists of extruding a film-forming material through a flat die over a chill roll, preferably immersed in water, to chill the molten film.

In the case of multilayer films the various polymers or blends of polymers are generally coextruded by conventional techniques but, when only a few of the layers have to undergo special treatments, such as for example irradiation with fast electrons to induce cross-linking, only the layer or layers to be treated is extruded or are coextruded, the tape obtained in

- 4 -

this way is subjected to the required treatment and then the remaining layers are extruded on the same.

The tape is then oriented, by stretching, in two separate and successive steps, although devices able to stretch the tape simultaneously in both directions are known (U.S. patent 3,148,409).

Generally stretching is performed first in machine direction (MD) and then in cross-direction (TD).

MD stretching is usually carried out by passing the tape through pairs of rolls which rotate at different speeds. At least one of the first pairs of rolls is heated, for example by inner circulation of hot oil.

TD stretching is usually performed in a tenter frame oven which comprises a certain number of heating zones and suitable stretching means.

Typically a tenter frame oven comprises from three to six zones: one to two for preheating the tape, one to two for stretching it in the cross-direction and one to two for relaxing and winding the film. Each zone may be heated at a different temperature level.

This technique has not however been adopted in the manufacture of heat shrinkable films based on ethylene copolymers.

Only EP-A-405 916 discloses the utilization of this technique in the manufacture of an extruded, bioriented, mono or multilayer film, wherein the film-forming polymers of at least one layer consist of:

(A) 75-100%, by weight, of at least one linear ethylene/alpha-olefin copolymer having a density of between 0.890 g/cm³ and 0.930 g/cm³, and

- 5 -

(B) 25-0%, by weight, of a linear high density polyethylene having a density of between 0.935 and 0.960 g/cm³, with the proviso that the total of the film-forming polymer (A) and (B) has a single melting point as determined by

5 differential scanning calorimetry according to ASTM D-3417.

Moreover, EP-A-405 916, page 3, lines 18-21, reports that attempts made to apply the tenter frame technique to the polymers of GB-A-2 097 324 have not given satisfactory results because the films obtained in this way were highly sensitive to

10 minimal variations of the process parameters, such as stretching temperature, stretching ratio and the speed of the manufacturing line.

Although EP-A-405 916 also refers to multilayer films, its examples only refer to monolayer films.

15 On the other hand, multilayer films have, compared to monolayer ones, the considerable advantage of allowing to combine one with the other several layers having different physical and chemical properties in view of the required properties of the final film.

20 Therefore the need for heat shrinkable multilayer films, extruded from a flat die, bioriented by the tenter frame technique, wherein at least one layer comprises ethylene copolymers, is still greatly felt.

In fact, the films manufactured by this technique have

25 several advantages over those manufactured by the air bubble technique.

A first advantage consists of the fact that the stretching ratios in machine direction and cross-direction may vary as required whereas in the air bubble technique they are always

30 substantially equal one to the other.

A second advantage is that the stretching ratio may be preselected within a relatively wide range, typically of between 2:1 and 12:1, while in the air bubble technique it must be between 3:1 and 6:1.

5 A third advantage is that the sealing agents can be selected as required whereas in the air bubble technique they have to be selected in the restricted range of sealants whose softening point is not substantially lower than the stretching
10 temperature to prevent the sealant from softening during the heating step, with consequent sealing of the opposite walls of the bubble.

A further advantage consists of the fact that the thickness and planarity of the films manufactured by this technique are much more uniform than in those manufactured with the air
15 bubble technique.

An additional advantage is that, being able to control the thickness better, thinner films can be manufactured, consequently saving materials and reducing environmental impact.

20 OBJECTS OF THE INVENTION

It is an object of the present invention to provide a multilayer heat shrinkable film which goes some way towards overcoming the disadvantages of the prior art, or at least to provide the public with a useful choice.

25 Accordingly, in a first aspect, the present invention provides a multilayer, bioriented, heat shrinkable thermoplastic film extruded from a flat die, wherein at least one layer comprises a copolymer ethylene/alpha olefin C_4-C_{12} characterized in that:

(a) said layer consists of
30 A₁) from 50 to 100 parts by weight of an ethylene/alpha-olefin C_4-C_{12} copolymer or a mixture of ethylene/alpha-olefin C_4-C_{12} copolymers, and

A₂) from 50 to 0 parts by weight of a polymer selected from polyolefins, modified polyolefins and mixtures thereof,

with the proviso that this layer shows more than one melting point when detected by differential scanning calorimetry according to ASTM D-3418,

(b) the total thickness variation in said multilayer film is lower than $\pm 10\%$.

5 (c) the average deviation (snaking) from straight line of the multilayer film is lower than ± 40 mm.

(d) the sag average of the multilayer film is lower than 25 mm.

10 In a second aspect, the present invention provides a process for manufacturing a multilayer, bioriented, heat shrinkable thermoplastic film, wherein a film according to the invention is obtained by stretching a tape at first in the machine direction at a temperature of from 60 to 150°C and then in cross direction by preheating at a temperature of from 80 to 190°C, stretching at a temperature of from 60 to 160°C and, finally, relaxing it at a temperature of from 50 to 150°C.

15 In a further aspect, the present invention provides a method for packaging an article wherein a multilayer, bioriented, heat shrinkable thermoplastic film according to the invention is wrapped around said article, sealed or clipped and shrunk.

DEFINITIONS

20 Unless otherwise stated, in this description and in the claims, the following symbols have the meanings set forth hereinbelow.

A. Extrusion

S_e = linear speed (m/min.) of the quenched cast film tape

T_c = chill roll temperature.

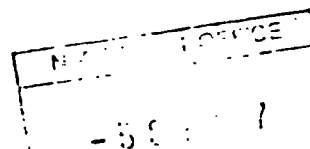
25 B. Longitudinal orientation

L_r = longitudinal stretching ratio

T_p = rolls temperature (°C) before longitudinal orientation (preheating)

T_l = rolls temperature (°C) during longitudinal orientation

30 MD = machine or longitudinal direction



- 8 -

C. Cross-direction orientation C_r = cross-direction stretching ratio T_{cp} = preheating temperature ($^{\circ}\text{C}$) in the cross-direction T_{cs} = stretching temperature ($^{\circ}\text{C}$) in the cross-direction5 T_{cr} = relaxation temperature ($^{\circ}\text{C}$) in the direction S_c = winding speed TD = cross-directionD. Properties of the films ST = shrink tension

10 This property is measured by gradually heating the film and measuring the maximum force developed per section unit of the film itself.

 SX = shrink percentage15 This property is measured by heating the film at 120°C for at least 5 sec., and then measuring the percentage of shrinkage in the longitudinal direction and in the cross-direction. H = haze

This property is measured according to ASTM D 1003-61.

20 G = Gloss

This property is measured according to ASTM D 2457-90.

 M = elastic modulus

This property is measured according to ASTM D 882-90.

15 σ = tensile strength

25 This property is measured according to ASTM D 882-90.

 E = elongation

This property is measured according to ASTM D 882-90.

 TTY = total thickness variation

This property is measured according to ASTM D 374-88.

30 PTV = planarity variation

- 9 -

The main planarity defects consist of bag & sag and snaking.

The device used to measure these defects essentially consists of

- 5 1. an unwind section with locking devices,
2. a dancing rolls to allow proper tension adjustment,
3. two idle rolls spaced circa 4 metres one from the other to support the film span under measurement,
4. a reference scale for proper film alignment close to
10 each idle roll,
5. a pair of rubber clamps actuated by a pedal lever to block the film side opposite to the unwind section,
6. a motorised rewind section,
7. a device for measuring the length of the rewound film
15 between two sets of measurement,
8. a guide, positioned substantially at the center between the two idle rolls, which supports:
 - a) a feeler fixed to a sliding support unit provided with a scale for measuring the horizontal distance
20 covered by the feeler from a prefixed zero point corresponding to the left edge of the film and a second scale for measuring vertical movements. The zero on this scale has been fixed by taking into consideration the natural drop midway in a perfectly
25 flat film span,
 - b) a slide fixed at the zero reference point,
9. various couples of weights to be attached to the dancing roller to adjust the tension of the film according to the type, width and thickness of the film itself.
- 30 In order to perform the measurements, a roll of film is

- 10 -

placed in the unwind section and a length of film is unwound.

The unwind station is locked.

The film is aligned and fixed to the wind-up core.

5 The rewind section is locked.

Using the vertical scale, the position of the flattest part of the film is measured.

10 The bag and sag in the film are then measured by recording the difference between the film levels at each point and the level of the flattest part of the film.

Measurements are taken along the whole film width from the left to the right side so as to obtain a representative profile of the surface. For this purpose measurements every 5-10 cm are recommended.

15 The data are reported on paper, i.e. sag and relevant position (left, center or right).

The whole operation is performed twice to four times to measure from two to four lengths of film.

20 Snaking, also referred to as "banana effect", represents the deviation of film from a straight line for a given length of material.

The measurements are performed on a length of film of 4 metres using the device and method described above.

Cross-linking is measured according to ASTM D 2765-90.

25 The term Mrad denotes the dose absorbed by the tape or by the film during treatment of irradiation with high energy electrons, and is equivalent to 10^4 J/Kg.

30 Moreover, unless otherwise stated in this description and in the claims, the following terms have the meanings indicated hereinbelow.

- 11 -

The term "film" means a flat and flexible material having a thickness of between 5 and 150 microns.

The term "heat shrinkable film" means a bioriented film which shrinks by at least 15% at 120°C in both directions.

5 The term "tape" means a layer of material before orientation and has typically a thickness of between 180 microns and 3 mm.

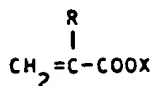
The term "polyolefin" means thermoplastic resins obtained by homopolymerisation or copolymerisation of olefins with other monomers, wherein the olefin units are present in larger
10 amounts than other monomers. The term "polyolefin" comprises but is not limited to "ethylene/alpha-olefin copolymer", "ethylene/vinyl acetate (EVA) copolymer", "ethylene/acrylate copolymer", "propylene copolymer" and "polypropylene" (PP) as defined hereinafter.

15 The term "modified polyolefins" means polyolefins characterised by the presence of functional groups, such as anhydride and/or carboxyl acid groups.

The term "ethylene/alpha-olefin copolymer" means a copolymer of ethylene and one or more C_4-C_{12} alpha-olefins and is
20 preferably selected from the group comprising linear copolymers of ethylene and butene-1, 4-methyl-pentene-1, hexene-1 or octene-1.

The term "ethylene/vinyl acetate (EVA) copolymer" means an ethylene/vinyl acetate copolymer wherein the ethylene units are
25 present in larger amounts than the vinyl acetate units.

The term "ethylene/acrylate copolymer" means a compound obtained by copolymerisation, according to known techniques, of ethylene with acrylic monomers of the formula



30

- 12 -

where R is H or C_1-C_4 alkyl, and

X is H, C_1-C_4 alkyl or a metal cation, preferably chosen from Zn^{++} and Na^+ ,

wherein the ethylene units are present in larger amounts than the acrylic units.

5 The term "propylene copolymer" means a copolymer of propylene and ethylene and/or butene-1 wherein the propylene units are present in larger amounts than the ethylene or butene units.

10 The term "polypropylene" (PP) means a thermoplastic resin obtained by homopolymerisation of propylene according to conventional techniques.

SUMMARY OF THE INVENTION

15 It has now been found that the abovementioned objects are achieved with a multilayer, bioriented, heat shrinkable film extruded from a flat die wherein at least one layer comprises an ethylene/alpha-olefin C_4-C_{12} copolymer, characterised in that said layer comprises

20 A₁) 50-100 parts, by weight, of an ethylene/alpha-olefin C_4-C_{12} copolymer or a blend of ethylene/alpha-olefin C_4-C_{12} copolymers, and

25 A₂) 50-0 parts, by weight, of a polymer selected from polyolefins, modified polyolefins and blends thereof, with the proviso that this layer has more than one melting point as determined by differential scanning calorimetry according to ASTM D-3418.

30 The present invention relates therefore to a multilayer, bioriented, heat shrinkable film extruded from a flat die wherein at least one layer comprises an ethylene/alpha-olefin C_4-C_{12} copolymer, characterised in that:

- 13 -

(a) said layer comprises

A₁) 50-100 parts by weight of an ethylene/alpha-olefin
C₄-C₁₂ copolymer or a blend of ethylene/alpha-olefin
C₄-C₁₂ copolymers, and

5 A₂) 50-0 parts by weight of a polymer chosen from among
polyolefins, modified polyolefins and blends thereof,
with the proviso that this layer has more than one melting
point as determined by differential scanning calorimetry
according to ASTM D-3418,

10 b) the total variation in thickness of said film is lower than
± 10%, and

c) the average deviation from a straight line (snaking) of said
film is less than 40 mm.

(d) the average sag is smaller than 25 mm.

15 The polyolefins are preferably selected from ethylene/vinyl
acetate copolymers, ethylene/acrylate copolymers, propylene
copolymers and polypropylenes.

The melting behaviour of ethylene/alpha-olefin C₄-C₁₂
copolymers depends on many factors related to the
20 copolymerisation process: quantity of the alpha-olefin, nature
of the catalyst, comonomer feed rate, temperature and other
process conditions which may have a significant effect on the
distribution of the alpha-olefin in the copolymer chains.

Examples of suitable alpha-olefins are butene-1,
25 4-methylpentene-1, hexene-1 and octene-1.

According to the present invention, the content of alpha-
olefin in the ethylene/alpha-olefin C₄-C₁₂ copolymer is
preferably of at least 7%, by weight, and the alpha-olefin is
octene-1.

30 Even more preferably the ethylene/alpha-olefin C₄-C₁₂

Advantageously the layers comprising an ethylene/alpha-olefin C_4-C_{12} copolymer are the core layer of a film having three layers or the skin layers of a film having five layers.

The method for manufacturing a multilayer, bioriented, heat shrinkable film according to the present invention comprises, preferably, stretching of the film, at appropriate temperatures, first in machine direction and then in cross-direction.

25 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 2 is a cross section a second preferred embodiment
30 according to the present invention consisting of a five-layer

- 15 -

bioriented film.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to Fig. 1, which is a cross section of a preferred
bioriented, three-layer film according to the present
invention, it can be seen that this embodiment comprises a core
layer 2 and two skin layers 1 and 3.

Preferably, the thickness of the film is of from 8 to 25
microns. The preferred thickness of the core or internal layer
is in the range of from 1 to 23 microns whereas that of each of
the skin (external) layers is in the range of from 1 to 12
microns.

The core layer comprises

A₁) 50-100 parts, by weight, of an ethylene/alpha-olefin C₄-C₁₂
copolymer or a blend of ethylene/alpha-olefin C₄-C₁₂
copolymers, and

A₂) 50-0 parts, by weight, of a copolymer chosen from among
ethylene/vinyl acetate copolymers, ethylene/acrylate
copolymers, polypropylenes, polypropylene copolymers,
modified polyolefins and blends thereof,

with the proviso that this layer has more than one melting
point as determined by differential scanning calorimetry
according to ASTM D-3418.

Typically, the core layer comprises 100%, by weight, of an
ethylene/alpha-olefin C₄-C₁₂ copolymer or a blend of
ethylene/alpha-olefin C₄-C₁₂ copolymers which have more than
one melting point as determined by differential scanning
calorimetry according to ASTM D-3418.

A typical example of film-forming composition suitable for
forming the layer 2 of Fig. 1 consists of 100% of an
ethylene/octene-1 copolymer which contains 10% of octene-1 and

- 16 -

has a density of 0.920 g/cm^3 and three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$.

When manufacturing a first preferred embodiment of Fig. 1, it may however be advantageous to recycle the remains of film-forming composition and scraps, of tape and/or film which are generated during the various steps of the manufacturing process, adding them to the film-forming composition of the core layer. In this case, the film-forming composition of the core layer will contain up to 25%, by weight, of a polymer chosen from polyolefins, modified polyolefins and blends thereof.

Preferably, both the skin layers 1 and 3 of Fig. 1 have the same composition and essentially consist of a polymer chosen from ethylene/vinyl acetate copolymers, ethylene/acrylate copolymers, polypropylenes, polypropylene copolymers, modified polyolefins and blends thereof.

Examples of preferred polyolefins for these layers are ethylene/alpha-olefin $\text{C}_4\text{-C}_{12}$ copolymers, propylene copolymers and polypropylenes.

A first typical example of a suitable film-forming composition for both layers 1 and 3 of Fig. 1 is the following:

- 40-60%, by weight, of a first ethylene/alpha-olefin $\text{C}_4\text{-C}_{12}$ copolymer,
- 20-30%, by weight, of a second ethylene/alpha-olefin $\text{C}_4\text{-C}_{12}$ copolymer,
- 20-30% by weight of an ethylene/vinyl acetate copolymer (EVA).

A second typical example of film-forming composition suitable for both layers 1 and 3 of Fig. 1 is the following:

- 75-100%, by weight, of a copolymer of propylene,

- 17 -

- 0-25%, by weight, of a polypropylene (PP).

The second preferred embodiment shown in Fig. 2 relates to a five-ply barrier film of this invention comprising a core layer 2, two tie (or intermediate) layers 4 and 5, and two skin layers 1 and 3.

Preferably, the thickness of this film is of from 15 to 45 microns.

The core layer 2 of the embodiment shown in Fig. 2 acts as a barrier against oxygen permeation and is made of any of the known barrier polymeric resins, such as ethylene/vinyl alcohol copolymers (EVOH) and vinylidene chloride copolymers (PVDC). The term EVOH refers to saponified products of ethylene/vinyl ester copolymers, generally of ethylene-vinyl acetate copolymers, wherein the ethylene content is typically comprised between 20 and 60% by mole and the degree of saponification is generally comprised between 85 and 99.5%. The EVOH can be employed as such or blended with other EVOHs or with one or more polyamides. The term PVDC refers to a vinylidene chloride copolymer wherein a major amount of the copolymer comprises vinylidene chloride and a minor amount of the copolymer comprises one or more unsaturated monomers copolymerizable therewith, typically vinyl chloride, and alkyl acrylates (e.g. methyl acrylate) or to a blend thereof in different proportions. Generally said PVDC will contain plasticisers and/or stabilizers as known in the art.

The composition of the two tie layers 4 and 5 of the embodiment shown in Fig. 2 may be the same or different. Advantageously the tie layers 4 and 5 have the same composition and are made of a modified polyolefin.

A typical example of film-forming composition suitable for

forming the layers 4 and 5 of Fig. 2 consists of 100% of a maleic anhydride grafted ethylene/butene copolymer containing 6% by weight of butene.

Preferably both skin layers 1 and 3 of the embodiment shown in Fig. 2 have the same composition and comprise

A₁) 50-100 parts, by weight, of an ethylene/alpha-olefin C₄-C₁₂ copolymer or a blend of ethylene/alpha-olefin C₄-C₁₂ copolymers, and

A₂) 50-0 parts, by weight, of a copolymer chosen from among polyolefins, modified polyolefins and blends thereof,

with the proviso that at least one of these layers has more than one melting point as determined by differential scanning calorimetry according to ASTM D-3418.

Typically, the skin layers 1 and 3 of the second preferred embodiment of Fig. 2 comprise 100%, by weight, of an ethylene/alpha-olefin C₄-C₁₂ copolymer or a blend of ethylene/alpha-olefin C₄-C₁₂ copolymers which have more than one melting point as determined by differential scanning calorimetry according to ASTM D-3418.

A typical example of a film-forming composition suitable for forming the layers 1 and 3 of Fig. 2 consists of 100% of an ethylene/octene-1 copolymer which contains 10% of octene-1 and has a density of 0.920 g/cm³ and three melting points at 106 ± 2; 119 ± 2 and 122 ± 2°C.

When manufacturing a second preferred embodiment according to Fig. 2, it may be advantageous to recycle the remains of film-forming composition and scraps, of tape and/or film, which are generated during the various steps of the manufacturing process, adding them to the film-forming composition for the skin layers 1 and 3 or, preferably, for the intermediate layers

- 19 -

4 and 5. Alternatively, and preferably in this case, additional inner layer(s) can be formed composed exclusively of recycled film. In any case the film will contain up to from 30% to 40% by weight, preferably up to 25%, even most preferably from about 7% to about 20% of recycled material.

A first specific example of composition suitable for manufacturing a multilayer, bioriented, heat shrinkable film according to the present invention is the following:

Film-forming composition of the core layer 2 (Fig. 1):

- 10 - 100% of an ethylene/octene-1 copolymer which contains 10% octene-1 (NMR determination) and has a density of 0.920 g/cm^3 and three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$.

Film-forming composition of the skin layers 1 and 3 (Fig. 1):

- 15 - 50.1%, by weight, of an ethylene/octene-1 copolymer which contains 10% of octene-1 (NMR determination) and has a density of 0.920 g/cm^3 and three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$;
- 20 - 24.8%, by weight, of an ethylene/octene-1 copolymer which contains 3.8% of octene-1 (NMR determination) and has a density of 0.926 g/cm^3 and a single melting point at $122.5 \pm 2^\circ\text{C}$;
- 25 - 24.6%, by weight, of an ethylene/vinyl acetate copolymer which contains 4.5% of vinyl acetate and has a density of 0.926 g/cm^3 and a single melting point at $106.8 \pm 2^\circ\text{C}$;
- 30 - 0.5% of slip and anti-block agents.

It will be noted that not only the core layer but also the skin layers have more than one melting point and come within the scope of the present invention also as regards their composition.

A second specific example is the following:

- 20 -

Film-forming composition of the core layer 2 (Fig. 1):

- 100% of an ethylene/octene-1 copolymer which contains 10% of octene-1 (NMR determination) and has a density of 0.920 g/cm^3 and three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$.

5 Film-forming composition of the skin layers 1 and 3 (Fig. 1):

- 87.5%, by weight, of a propylene/ethylene copolymer which contains 3.5% of ethylene and has a density of 0.900 g/cm^3 and a single melting point at 135.9°C ;
- 12.1%, by weight, of polypropylene having a density of 0.904 g/cm^3 and a single melting point at 160°C ;
- 0.4% of slip and anti-block agents.

A third specific example of composition suitable for manufacturing a multilayer, bioriented, heat shrinkable film according to the present invention is the following:

15 Film-forming composition of the core layer 2 (Fig. 2):

- 80% by weight of an ethylene/vinyl alcohol copolymer containing 44% ethylene,
- 20% by weight of a caprolactam/lauro lactam copolymer melting at $128\text{--}132^\circ\text{C}$;

20 Film forming composition of the intermediate layers 4 and 5 (Fig. 2):

- 100% by weight of a maleic anhydride grafted ethylene/butene copolymer containing 6% by weight of butene;

Film-forming composition of the skin layers 1 and 3 (Fig. 2):

- 25 - 50.1%, by weight, of an ethylene/octene-1 copolymer which contains 10% of octene-1 (NMR determination) and has a density of 0.920 g/cm^3 and three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$;
- 24.8%, by weight, of an ethylene/octene-1 copolymer which
- 30 contains 3.8% of octene-1 (NMR determination) and has a

- 21 -

density of 0.926 g/cm^3 and a single melting point at $122.5 \pm 2^\circ\text{C}$;

- 24.6%, by weight, of an ethylene/vinyl acetate copolymer which contains 4.5% of vinyl acetate and has a density of 0.926 g/cm^3 and a single melting point at $106.8 \pm 2^\circ\text{C}$;
- 0.5% of slip and anti-block agents.

It will be noted that the skin layers 1 and 3 have more than one melting point and come within the scope of the present invention.

10 Examples of suitable slip agents are erucamide (available from Humko Chemical under the trademark Kemamide E). Other examples of suitable slip agents are stearamide (available from Humko Chemical under the trademark Kemamide S) and N,N'-diole-

15 oylethylenediamine (available from Glyco Chemical under the trademark Acrawax C).

20 An example of a suitable anti-block agent is represented by diatomaceous silica (available from McCullough & Benton, Inc. under the trademark Superfine Superfloss). Other suitable anti-block agents are synthetic silicas such as those

25 manufactured and sold by the Davison Division of WR Grace, under the trademark Syloid.

As is well-known to those skilled in the art, other suitable additives for film-forming compositions are antioxidants, heat stabilisers, organic or inorganic coloured pigments, anti-fog

30 agents, anti-static agents, UV absorbers and the like.

These types of additives may be added to the film-forming compositions of the present invention according to criteria which are well-known to those skilled in the art, without however departing from the scope of the present invention.

30 In a typical embodiment of the present invention, the

- 22 -

extruded and cooled tape is irradiated, before stretching, with high energy electrons. Said irradiation may however also be performed during or after stretching.

As is well-known to those skilled in the art, this type of irradiation causes cross-linking of the polymers and improves their mechanical properties, especially at high temperatures.

The preferred level of radiation is of from 1 to 12 Mrad.

Even more preferably the level of radiation is of from approximately 1.5 to approximately 5 Mrad.

The preferred conditions for orienting the multilayer films of the present invention comprise first of all stretching in machine direction at a temperature of from 60 to 150°C, preferably of from 80 to 120°C, and then stretching in cross-direction, preheating the film to a temperature of from 80 to 190°C, preferably of from 110 to 170°C, stretching it at a temperature of from 60 to 160°C, preferably of from 80 to 140°C, and, finally, relaxing it at a temperature of from 50 to 150°C, preferably of from 75 to 130°C.

Generally, the stretching ratios according to the invention range from 2:1 to 11:1 in machine direction and from 3:1 to 12:1 in cross-direction and, preferably, from 4.5:1 to 9.5:1 in machine direction and from 5:1 to 11:1 in cross-direction.

Unlike multilayer, bioriented, heat shrinkable films manufactured with the same composition but by the air bubble technique, the multilayer, bioriented, heat shrinkable film of the present invention is characterised by a total thickness variation lower than $\pm 10\%$. Typically said total variation in thickness is lower than $\pm 5\%$.

Moreover, the film according to the present invention is characterised in that the average deviation from a straight

- 23 -

line (snaking) is smaller than 40 mm and that the average sag is smaller than 25 mm.

Typically, the average deviation from a straight line (snaking) is smaller than 25 mm.

5 The preferred use of the multilayer, bioriented, heat shrinkable film according to the present invention consists of packaging articles of various types. Preferably food products and consumer articles.

10 In practice, the film is wound around the article, sealed or clipped and shrunk according to conventional techniques. For example, by exposing the article wound in the film to a current of hot air or hot water.

The following examples are intended to illustrate the present invention without however limiting it in any way. The
15 melting points set forth in the description, in the claims and in the following examples have been measured by differential scanning calorimetry according to ASTM D-3418.

EXAMPLES 1-5

Film-forming composition of the core layer 2 (Fig. 1):

- 20 - 100% of an ethylene/octene-1 copolymer which contains 10% of octene-1 (NMR determination) and has a density of 0.920 g/cm^3 and three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$.

Film-forming composition of the skin layers 1 and 3 (Fig. 1):

- 25 - 50.1%, by weight, of an ethylene/octene-1 copolymer which contains 10% of octene-1 (NMR determination) and has a density of 0.920 g/cm^3 and three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$;
- 24.8%, by weight, of an ethylene/octene-1 copolymer which contains 3.8% of octene-1 (NMR determination) and has a
30 density of 0.935 g/cm^3 and a single melting point at $122.5 \pm$

- 24 -

2°C;

- 24.6%, by weight, of an ethylene/vinyl acetate copolymer which contains 4.5% of vinyl acetate and has a density of 0.926 g/cm³ and a single melting point at 106.8 ± 2°C;

5 - 0.5% of slip and anti-block agents.

Note: the aforesaid blend of layers 1 and 3 has two melting points at 102.1 and 120.5 ± 2°C.

Production was performed on Brueckner lines.

10 The film-forming compositions were coextruded through a flat die and the cast tape was chilled on a chill roll partially immersed in a water bath at a temperature of from 5 to 60°C (T_c) with the aid of an air knife. The linear speed of the quenched tape was of from 6 to 8 m/min (S_c).

15 The tape was then heated to a temperature of from 110 to 115°C on oil heated rolls stretching the tape in machine direction with ratios of from 6:1 to 9.5:1.

20 The tape was then transferred to a tenter frame oven having four heating zones in which the temperature was of from 115 to 130°C and then, in examples 1, 3, 4, 5, in a stretching zone heated to temperatures of from 115°C to 127°C, with stretching ratios of from 5.8:1 to 6.1:1 and finally in a relaxation zone heated to a temperature of from 80 to 85°C.

In example 2, 2 stretching zones and no relaxation zone were used.

25 Finally the film was cooled and wound onto a roll at a speed of from 30 to 50 m/min. (S_c).

The multilayer bioriented films obtained in this way have a thickness of 15 microns.

The ratio between layers 1, 2 and 3 was 1:2:1, respectively.

30 The process conditions (PC) of Examples 1-5 and the physical

- 25 -

properties (FA) of the films manufactured are shown in Table A below.

COMPARATIVE EXAMPLE 1

5 By way of a comparison, with the film-forming compositions of Examples 1-5 a three-layer bioriented film was manufactured by the air bubble technique, proceeding as described hereinafter.

The film-forming compositions were coextruded in the form of a tube.

10 After quenching and solidification, the extruded tube was heated and inflated into a bubble by applying an internal air pressure and thus transforming the narrow, thick-walled tube into a wide, thin-walled tube.

15 After this stretching step, the tubular film was cooled and collapsed into a superimposed lay-flat tape and wound onto cylinders.

The air bubble process orients the film by stretching it simultaneously both longitudinally and transversely, thus imparting shrinkability.

20 The comparison film obtained in the best working conditions known to the inventors had a thickness of 15 microns and will be denoted hereinbelow by the code C-1.

25 The physical properties (FA) of the film C-1 and the working conditions of its manufacturing process (PC) are shown in Tables A-F below in comparison with those of films of the present invention.

EXAMPLES 6-9

30 The film-forming composition of examples 1-5 was used, changing the stretching conditions as shown in Table B which also shows the properties of the films obtained in this way.

- 26 -

EXAMPLES 10-12

The film-forming composition of examples 1-5 was used, changing the stretching conditions as shown in Table C which also shows the properties of the films obtained in this way.

5 More particularly the MD and TD shrinkage values, which may differ one from the other within a wide range, are worthy of note.

EXAMPLES 13-14

10 The film-forming composition of examples 1-5 was used, changing the stretching conditions as shown in Table D which also shows the properties of the films obtained in this way.

More particularly, the chain configuration for TD orientation was modified as follows:

- 15 - in Example 13, 4 zones of the tenter frame oven have been devoted to preheating, 2 zones to stretching and no zone to relaxation;
- in Example 14, 1 zone of the tenter frame oven has been devoted to preheating, 2 zones to stretching and 3 zones to relaxation.

20 The data in Table D clearly show that, by increasing the number of zones of relaxation, the TD shrink tension can be reduced without affecting the high shrinkage values.

EXAMPLES 15-16

25 The film-forming composition of examples 1-5 was used, changing the stretching conditions as shown in Table E which also shows the properties of the films obtained in this way.

The data in Table E show that lower shrink tension values can be obtained, especially in TD.

EXAMPLE 17

30 The film-forming composition of examples 1-5 was used,

- 27 -

increasing the manufacturing line speed to reduce the thickness of the film to 10 microns and also changing the stretching conditions as shown in Table F which also shows the properties of the films obtained in this way compared with the film C-1 which is 15 microns thick.

The data in Table F show that, in spite of the smaller thickness, the film of the present invention has greater shrinkage values.

EXAMPLES 18-20

The film-forming composition of examples 1-5 was used, changing the stretching conditions as indicated in Table G which also reports the properties of the thus obtained films. In examples 19 and 20 the manufacturing line speed was also increased to reduce the thickness of the films to 12 and 10 microns respectively. The same configuration of the tenter frame oven has been employed in these three examples: 2 preheating zones, 2 stretching zones and 2 relaxation zones.

The physical properties (FA) of the films and the working conditions of their manufacturing process (PC) are shown in Table G.

EXAMPLES 21-23

The following film-forming compositions were used.

Film-forming composition of the core layer 2 (Fig. 1):

- 100% of an ethylene/octene-1 copolymer which contains 10% octene-1 (NMR determination) and has a density of 0.920 g/cm^3 and three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$.

Film-forming composition of the skin layers 1 and 3 (Fig. 1):

- 87.5%, by weight, of a propylene/ethylene copolymer which contains 3.5% ethylene and has a density of 0.900 g/cm^3 and a single melting point at $135.9 \pm 2^\circ\text{C}$;

- 28 -

- 12.1%, by weight, of polypropylene having a density of 0.904 g/cm³ and a single melting point at 160 ± 2°C;
- 0.4% of slip and anti-block agents.

Note: the abovementioned blend of layers 1 and 3 has one melting point at 128 ± 2°C.

The procedure of Examples 1-5 was used, changing the stretching conditions as shown in Table H which also shows the properties of the films obtained in this way, together with those of the comparison film C-2 (see comparative example 2 below).

The ratio between layers 1, 2 and 3 was 1:3:1, respectively.

The data of Table H show that the working conditions of the manufacturing process of the invention may change within very wide ranges.

COMPARATIVE EXAMPLE 2

By way of a comparison, with the film-forming compositions of Examples 21-23, a three-layer bioriented film was manufactured with the air bubble technique, working under the best conditions known to the inventors. The film manufactured in this way had a thickness of 15 microns and is denoted hereinunder by the code C-2. The physical properties (FA) of the film C-2 and the working conditions of its manufacturing process (PC) are shown in Table H in comparison with those of the films of Examples 21-23 of the invention.

EXAMPLE 24

The following film-forming compositions have been used:

Film-forming composition of the core layer 2 (Fig. 1):

as indicated for the core layer of examples 21-23;

Film-forming composition of the skin layers 1 and 3 (fig. 1):

- 87.5%, by weight, of a propylene-ethylene-butene-1 terpolymer

- 29 -

containing 94% propylene, 4% ethylene and 2% butene-1, m.p.
130 \pm 2°C;

- 12.1%, by weight, of polypropylene having a density of 0.904
g/cm³ and m.p. 160 \pm 2°C;

5 - 0.4% of slip and anti-block agents.

The ratio between layers 1, 2 and 3 was 2:11:2 respectively.

The same general process described in examples 1-5 was used,
changing however the stretching conditions as indicated in
Table I which also reports the properties of the films thus
10 obtained.

EXAMPLE 25

The following film-forming compositions have been used:

Film-forming composition of the core layer 2 (Fig. 1):

as indicated for the core layer of examples 21-23;

15 Film-forming composition of the skin layers 1 and 3 (Fig. 1):

- 87.5%, by weight, of a propylene-ethylene-butene-1 terpolymer
containing 91% propylene, 2% ethylene and 7% butene-1, m.p.
126 \pm 2°C;

20 - 12.1%, by weight, of polypropylene having a density of 0.904
g/cm³ and m.p. 160 \pm 2°C;

- 0.4% of slip and anti-block agents.

The ratio between layers 1, 2 and 3 was 2:11:2 respectively.

The same general process described in examples 1-5 was used,
changing however the stretching conditions as indicated in
Table I which also reports the properties of the films thus
25 obtained.

EXAMPLE 26

The following 5-ply barrier film was prepared by following
the general process of examples 1-5 but using the film forming
30 compositions indicated below:

- 30 -

Film-forming composition of the core layer 2 (Fig. 2):

- 80%, by weight, of an ethylene-vinyl alcohol copolymer containing 44% ethylene;
- 20%, by weight, of a caprolactam/lauryl lactam copolymer with m.p. 128-132°C;

5

Film-forming composition of the skin layers 1 and 3 (Fig. 2):

- the same blend used for the skin layers 1 and 3 in examples 1-5;

Film-forming composition of the intermediate layers (tie

10

layers) on both sides of the core layer 4 and 5 (Fig. 2):

- maleic anhydride grafted ethylene-butene copolymer containing 6% by weight of butene.

The ratio between the five layers was 2:2:1:2:2.

The line speed was adjusted to get a film 25 microns thick.

15

The stretching ratios, the stretching conditions and the properties of the thus obtained film are reported in Table I.

20

25

30

TABLE A													
Films of the samples													
PS	1	2	3	4	5	6	7	8	9	10	11	12	13
L _r	6:1	6:1	6:1	8:1	9.5:1	5:1							
T _p (°C)	115	115	115	110	110	-							
T _l (°C)	115	90	110	115	115	115							
L _c	6:1	6:1	6:1	5.7:1	5.8:1	5:1							
T _{cp} (°C)	115	115	115	127	127	-							
T _{cs} (°C)	115	115-80	115	127	127	115							
ISF (°C)	10	-	80	85	85	-							
FA	MD	TD	MD	TD	MD	TD	MD	TD	MD	TD	MD	TD	MD
ST Kg/cm ²	17.8	35.5	21.9	39.7	29.4	38.0	37	21	44	19	22.4	27.31	
SX 120 (°C)	58	73	64	66	65	67	67	57	66	56	60	64	
H	3.6	2.2	1.7	1.7	-	-	-	-	-	-	-	2.4	
G	132	139	142	-	-	-	-	-	-	-	-	137	
M Kg/cm ²	4279	5400	4221	5048	4644	5766	-	-	-	-	3558	34571	
TS Kg/cm ²	1015	946	1356	1302	1494	1337	-	-	-	-	1194	11141	
LE	103	138	112	102	101	117	-	-	-	-	100	1101	
Average													
thickness μ	14.1	15.2	14.9	15.8	16.0	15.0							
TTV μ	41	41	41.1	40.9	41.6	43							
PTV sag mm	25	20	22	-	-	35							
stretching mm	15	20	22	-	-	21							

TABLE 8 Values of the parameters											
PC	6	7	8	9	5-1						
L _r	6:1	6:1	6:1	6:1	5:1						
T _p (°C)	115	115	115	100	-						
T _l (°C)	115	115	90	95	115						
T _c	6:1	6:1	6:1	7.3:1	5:1						
T _{cp} (°C)	115	117	116	130	-						
T _{cs} (°C)	115	115	115	125-95	115						
ISC (°C)	80	115-80	115-80	85	-						
FA	MD	TD	MD	TD	MD	TD	MD	TD	MD	TD	TD
ST Kg/cm ²	17.7	35	20.4	24.4	13.9	33.8	10	37	22.4	27.31	
SX 120 (°C)	58	73	62	66	61	68	56	63	60	64	
H	2.5		2.2		1.7		-	-	-	2.4	
G	137		138		144		-	-	-	137	
M Kg/cm ²	5068	5409	5056	5912	4462	5816	-	-	3558	3457	
TS Kg/cm ²	914	1116	1216	125	1160	1661	-	-	1194	1114	
E	110	110			125	85	-	-	100	110	
Average											
thickness μ	14.8		15.1		15.0		14.9		15.0		
TTV μ	41		41.4		40.8		40.9		43		
PTV sag mm	23		21		-		-		35		
soaking mm	20		20		-		-		31		

SECRET

TABLE 5											
Films of the Examples											
PG	10	11	12	13	14	15	16	17	18	19	20
L _r	4.5:1	4.5:1	4.5:1	4.5:1	4.5:1	4.5:1	4.5:1	4.5:1	4.5:1	4.5:1	4.5:1
T _p (°C)	100	100	100	100	100	100	100	100	100	100	100
T _p (°C)	85	95	95	95	95	95	95	95	95	95	95
T _c	6.2:1	6.2:1	6.2:1	6.2:1	6.2:1	6.2:1	6.2:1	6.2:1	6.2:1	6.2:1	6.2:1
T _p (°C)	134	134	134	134	134	134	134	134	134	134	134
T _p (°C)	115-95	115-95	115-95	115-95	115-95	115-95	115-95	115-95	115-95	115-95	115-95
T _c	95	95	95	95	95	95	95	95	95	95	95
T _c (°C)	7.1	6.1	9.4	9.3	14.3	14.3	14.3	14.3	14.3	14.3	14.3
ST Kg/cm ²	20	52	56	56	38	38	38	38	38	38	38
SX 120 (°C)	20	52	56	56	38	38	38	38	38	38	38
H	6.1	6.1	7.1	7.1	6.4	6.4	6.4	6.4	6.4	6.4	6.4
G	122	122	119	119	119	119	119	119	119	119	119
M Kg/cm ²	2847	3539	3117	3575	3255	3255	3255	3255	3255	3255	3255
TS Kg/cm ²	475	377	536	381	1117	1117	1117	1117	1117	1117	1117
E	270	176	263	120	165	165	165	165	165	165	165
Average											
thickness μ	16.0		15.3		14.8						15.0
TTV μ	21.1		21.4		20.8						23
PTV sag mm	-		-		-						35
snaking mm	-		-		-						51

TABLE D
Films of the Examples

PC	13	14	15
L _r	6.1	6.1	5:1
T _p (°C)	115	115	-
T _p (°C)	90	115	115
T _c (°C)	6:1	6:1	5:1
T _c (°C)	115	117	-
T _c (°C)	115-80	115	115
T _c (°C)	115-80	115-80	-
Is _c (°C)	115-80	115-80	-
EA	MD	TD	MD
ST Kg/cm ²	15.8	54.7	27.8
SX 120 (°C)	58	68	60
H	1.7	1.8	2.4
G	143	140	137
M Kg/cm ²	6039	4632	3657
TS Kg/cm ²	1273	2011	1194
E	140	63	100
Average	15.1	14.3	15.0
thickness μ	21.2	20.8	23
TIV μ	18	25	35
PTV sag mm	20	23	21

TABLE I									
Films of the Examples									
PC	12	16	5-1						
L _r	6.1	6.1	5:1						
T _p (°C)	100	100	-						
T _l (°C)	95	85	115						
L _c	5:1	5:1	5:1						
T _r (°C)	134	134	-						
T _{cp} (°C)	115-105	115-95	115						
T _{cs} (°C)	85	85	-						
T _{cr} (°C)	85	85	-						
FA	MD	TD	MD	TD	MD	TD			
ST Kg/cm ²	14.7	2.3	13.9	3.5	22.4	27.3			
SK 120 (°C)	44	47	36	46	60	64			
H	10.3			12	2.4				
G	104			98	137				
M Kg/cm ²	3761	4194	3509	3738	3558	3457			
TS Kg/cm ²	1378	442	1411	419	1194	1114			
E	122	240	117	268	100	110			
Average									
thickness μ	14.1		15.6		15.0				
TTV μ	40.8		41.5		43				
PTV sag mm	-		-		35				
ingering mm	-		-		51				

TABLE I
Films of the Examples

PS	17	5-1
L _r	6.1	5:1
T _p (°C)	115	-
T _l (°C)	115	115
C _r	6:1	5:1
T _{cp} (°C)	115	-
T _{cs} (°C)	115	115
T _{cr} (°C)	80	-
FA	MD	TD
ST Kg/cm ²	30.5	34.0
SX 120 (°C)	67	69
H	1.2	2.4
G	15	137
M Kg/cm ²	4896	5342
TS Kg/cm ²	1503	1287
S	86	112
Average		100
Thickness μ	10.1	15.0
TIV μ	20.8	33
PIV sag mm	-	35
spotting mm	-	51

TABLE 6									
Filling of the Samples									
PS	18	19	20						
L _r	5.5:1	5.5:1	5.5:1						
T _r (°C)	110	110	110						
P	90	90	90						
T _i (°C)	90	90	90						
L _c	8.5:1	8.5:1	8.5:1						
T _c	130	130	130						
T _{cp} (°C)	118	118	118						
T _s (°C)	90	90	90						
ISC (°C)	90	90	90						
FA	MD	MD	MD						
ST Kg/cm ²	--	--	--						
SX 120 (°C)	51	51	55						
H	3.4	3.8	4.2						
G	128	127	118						
M Kg/cm ²	4780	5220	7800						
TS Kg/cm ²	103	1180	1420						
E	109	100	85						
Average									
thickness μ	15.1	12.3	9.9						
TTV μ	11.0	10.9	10.7						
PIV 100 mm	23	18	21						
inletting mm	20	16	18						

TABLE H
filling of the frames

PC	21	22	23	24
L _r	5:1	7:1	6:1	5:1
T _r (°C)	100	100	100	-
P	90	90	90	115
T _l (°C)	5:1	7:1	8.4:1	5:1
C _r	148	148	162	-
T _{cp} (°C)	130	130	130	115
T _{cs} (°C)	110	110	110	-
FA	MD	TD	MD	TD
ST kg/cm ²	9.7	11.6	11.4	17.4
SX 120 (°C)	32	32	29	43
H	8.1	9.5	7.5	1.9
G	102	122	130	138
M kg/cm ²	5260	7662	6930	8080
TS kg/cm ²	610	868	803	919
E	107	84	89	108
Average	15.5	15.9	16.1	15.0
Thickness μ	21.2	21.4	21.5	23
PTV sag mm	24	25	23	35
sinking mm	28	32	20	24

TABLE I Values of the Examples									
PC	24	25	26						
L _r	6.5:1	6.5:1	2.4:1						
T _p (°C)	115	115	110						
T _l (°C)	110	100	90						
T _c	6.5:1	6.5:1	4.5:1						
T _{cp} (°C)	145	140	118						
T _{cs} (°C)	120	111	115						
T _{sc} (°C)	95-80	88-70	110						
FA	MD	TD	MD	TD	MD	TD			
ST Kg/cm ²	--	--	--	--	--	--			
SX 120 (°C)	31	44	35	52	24	56			
H	4.0			1.7		3.4			
G	123			122		128			
M Kg/cm ²	4700	5600	6031	7245	6629	7496			
TS Kg/cm ²	580	490	927	540	600	850			
E	90	60	87	34	209	92			
Average									
Thickness μ	15.3			15.8		25.3			
ITV μ	30.9			31.1		41.1			
PTV sag mm	18			--		24			
spotting mm	19			--		20			

CLAIMS

1. A multilayer, bioriented, heat shrinkable thermoplastic film extruded from a flat die, wherein at least one layer comprises a copolymer ethylene/alpha olefin C_4-C_{12} characterized in that:

(a) said layer consists of

A₁) from 50 to 100 parts by weight of an ethylene/alpha-olefin C_4-C_{12} copolymer or a mixture of ethylene/alpha-olefin C_4-C_{12} copolymers, and

A₂) from 50 to 0 parts by weight of a polymer selected from polyolefins, modified polyolefins and mixtures thereof,

with the proviso that this layer shows more than one melting point when detected by differential scanning calorimetry according to ASTM D-3418,

(b) the total thickness variation in said multilayer film is lower than $\pm 10\%$.

(c) the average deviation (snaking) from straight line of the multilayer film is lower than ± 40 mm.

(d) the sag average of the multilayer film is lower than 25 mm.

2. A multilayer film according to claim 1, wherein the total thickness variation is lower than $\pm 5\%$.

3. A multilayer film according to claim 1 or 2, wherein the average deviation (snaking) from straight line is lower than ± 25 mm.

4. A multilayer film according to anyone of claims from 1 to 3, characterized in that it has been stretched with a stretching ratio of from 2:1 to 11:1 in machine direction and of from 3:1 to 12:1 in cross direction.

5. A multilayer film according to claim 4, characterized in that it has been stretched with a stretching ratio of from 4.5:1 to 9.5:1 in machine direction and of from 5:1 to 11:1 in cross direction.
- 5 6. A multilayer film according to anyone of claims from 1 to 5, wherein polyolefins are selected from ethylene/vinyl acetate copolymers, ethylene/ acrylates copolymers, propylene copolymers and polypropylenes.
- 10 7. A multilayer film according to anyone of claims from 1 to 6, wherein the amount of alpha-olefin in the ethylene/alpha-olefin C_4-C_{12} copolymer is of at least 7% by weight.
8. A multilayer film according to claim 7, wherein the alpha-olefin is octene-1.
- 15 9. A multilayer film according to claim 8, wherein the amount of octene-1 is of $10\% \pm 2\%$ by weight.
10. A multilayer film according to claim 8, wherein the ethylene/octene-1 copolymer has a density of about 0.920 gr/cm^3 .
- 20 11. A multilayer film according to claims 9 or 10, wherein the ethylene/octene-1 copolymer has three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$.
12. A multilayer film according to anyone of claims from 1 to 11, characterized in that it is cross-linked.
- 25 13. A multilayer film according to claim 12, wherein the cross-linking has been performed by irradiation with high energy electrons at an irradiation level of from 1 to 12 Mrad.
- 30 14. A multilayer film according to anyone of claims from 1 to 13, wherein the layer comprising an ethylene/alpha-olefin

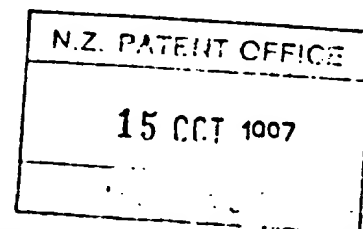
- C_4-C_{12} copolymer is the core layer of a three-layer film.
15. A multilayer film according to anyone of claims from 1 to 14, wherein the two outside layers have the same composition consisting of a polymer selected from ethylene/alpha-olefin C_4-C_{12} copolymers, ethylene/vinyl acetate copolymers, ethylene/acrylates copolymers, polypropylene copolymers, polypropylenes, modified polyolefins and mixtures thereof.
16. A multilayer film according to claim 15, wherein the two outside layers comprise
- from 40 to 60% by weight of a first ethylene/alpha-olefin C_4-C_{12} copolymer,
 - from 20 to 30% by weight of a second ethylene/alpha-olefin C_4-C_{12} copolymer,
 - from 20 to 30% by weight of an ethylene/vinyl acetate copolymer (EVA).
17. A multilayer film according to claim 16, wherein the first ethylene/alpha-olefin C_4-C_{12} copolymer is an ethylene/octene-1 copolymer.
18. A multilayer film according to claim 17, wherein the first copolymer contains $10\% \pm 2\%$ by weight of octene-1.
19. A multilayer film according to claims 17 or 18, wherein the first ethylene/octene-1 copolymer has a density of about 0.920 gr/cm^3 .
20. A multilayer film according to anyone of claims from 17 to 19, wherein the first ethylene/octene-1 copolymer has three melting points at 106 ± 2 ; 119 ± 2 and $122 \pm 2^\circ\text{C}$.
21. A multilayer film according to anyone of claims from 17 to 20, wherein the second ethylene/alpha-olefin C_4-C_{12} copolymer is an ethylene/octene-1 copolymer.

22. A multilayer film according to claim 21, wherein the second ethylene/octene-1 copolymer contains from 2.5 to 4.5% by weight of octene-1.
23. A multilayer film according to claims 21 or 22, wherein the second ethylene/octene-1 copolymer has a density of about 0.935 gr/cm³.
24. A multilayer film according to anyone of claims from 21 to 23, wherein the second ethylene/octene-1 copolymer melts at 122.5 ± 2°C.
25. A multilayer film according to anyone of claims from 21 to 24, wherein EVA has a density of about 0.926 gr/cm³.
26. A multilayer film according to anyone of claims from 21 to 25, wherein EVA melts at 106.8 ± 2°C.
27. A multilayer film according to claim 15, wherein the two outside layers comprise
- from 75 to 100% by weight of a propylene copolymer,
 - from 0 to 25% by weight of a polypropylene (PP).
28. A multilayer film according to claim 27, wherein the propylene copolymer has a density of about 0.900 gr/cm³.
29. A multilayer film according to claims 27 or 28, wherein the propylene copolymer melts at from 125 to 138°C.
30. A multilayer film according to anyone of claims from 27 to 29, wherein PP has a density of about 0.904 gr/cm³.
31. A multilayer film according to anyone of claims from 27 to 30, wherein PP melts at 160 ± 2°C.
32. A multilayer film according to anyone of claims from 1 to 13, wherein the layer comprising an ethylene/alpha-olefin C₄-C₁₂ copolymer is a skin layer of a five-layer film.
33. A multilayer film according to claim 32, wherein the core layer of a five-layer film is an oxygen barrier layer.

276069

- 5 34. A process for manufacturing a multilayer, bioriented, heat shrinkable thermoplastic film, wherein a film according to anyone of claims from 1 to 32 is obtained by stretching a tape at first in the machine direction at a temperature of from 60 to 150°C and then in cross direction by preheating at a temperature of from 80 to 190°C, stretching at a temperature of from 60 to 160°C and, finally, relaxing it at a temperature of from 50 to 150°C.
- 10 35. A process according to claim 34, wherein the tape is stretched at first in the machine direction at a temperature of from 80 to 120°C and then in cross direction by preheating at a temperature of from 110 to 170°C, stretchig at a temperature of from 80 to 140°C and, finally, relaxing it at a temperature of from 75 to 130°C.
- 15 36. A method for packaging an article wherein a multilayer, bioriented, heat shrinkable thermoplastic film according to any one of claims from 1 to 33 or prepared by a process according to claim 34 or 35 is wrapped around said article, sealed or clipped and shrunk.
- 20 37. A multilayer, bioriented, heat shrinkable thermoplastic film as claimed in claim 1 substantially as herein described with reference to any example thereof and/or the accompanying drawings.
- 25 38. A process for manufacturing a multilayer, bioriented, heat shrinkable thermoplastic film as claimed in claim 34 substantially as herein described with reference to any example thereof and/or the accompanying drawings.
- 30 39. A method for packaging an article as claimed in claim 36 substantially as herein described with reference to any example thereof and/or the accompanying drawings.

END OF CLAIMS



Intellectual Property Details

Patent Number	276069
International Application Number	EP94/03589
WO Publication Number	95/13187
Patent Type	Patent PCT Inward
Current Status	Granted and Sealed
Patent Title	Multilayered, bioriented, heat shrinkable film

Documents

Abstract/Abridgement

Document

Requests - eg Antedating

ARev request info: Request_number = 504722

IP with assignment request

PSPRS ARev request: Subsequent proprietor by subprop S84(1) - trademark numbers for this request are: 203319, 203578, 204018, 205032, 205515, 205579, 205784, 207978, 209123, 209661, 210022, 211558, 212823, 213313, 214460, 214780, 215261, 215455, 215714, 217046, 230858, 230857, 217466, 217814, 218328, 218990, 219368, 219870, 219894, 220092, 220292, 220316, 220386, 220387, 221629, 231592, 222052, 222331, 222348, 222424, 222425, 222426, 222810, 223023, 223739, 223960, 224103, 225191, 225216, 226196, 226261, 226389, 226394, 226752, 226924, 226983, 227009, 227233, 227261, 227260, 227901, 228095, 228494, 231338, 231410, 231425, 231427, 232494, 232709, 232708, 232780, 233834, 234530, 235495, 236024, 236100, 236144, 234319, 236328, 236358, 235359, 236437, 237152, 237229, 237382, 234420, 237511, 237977, 237981, 238014, 238180, 239081, 239248, 239336, 239460, 239560, 239561, 240188, 240353, 241024, 241200, 239071, 241802, 242340, 242460, 242598, 242597, 243077, 243109, 244002, 245535, 245542, 247067, 247191, 247192, 247940, 248205, 280527, 248250, 248251, 248306, 248674, 256613, 256614, 248839, 248840, 248887, 248918, 248962, 248975, 248976, 248997, 250009, 250047, 250119, 250524, 250636, 250835, 250999, 260083, 260120, 260121, 260354, 260402, 260403, 260564, 260565, 264026, 264029, 264091, 264441, 274358, 276069, 279603, 270397, 270596, 328318, 270813, 283867, 283912, 284938, 270984, 272049, 272083, 272187, 272284, 272328, 272446, 272598, 272738, 272780, 280007, 280151, 280193, 280207, 280404, 280441, 280447, 280532, 280559, 280601, 280804, 286078, 311293, 286815, 299199, 299915, 314315, 314663, 328514, 282820, 289619, 298960, 305371, 310139, 311271, 312951, 315429, 321050, 321150, 331362, 331414, 331862, 332182, 314583, 330074, 333174, 333173, 333439, 333561, 333649, 333942, 328445, 333943, 333940, 333941, 333973, 332843, 332842, 329927, 331988

Supplementary information

Client Reference is: M387277 TJH/reb for party 203944, interest OWN, request 504722

Supplementary information

Client Reference is: M387277 TJH/reb for request 504722

Class

Classification **Schedule and Edition**
IPC|B32B27/32 IPC1
IPC|B65D65/40 IPC1

Dates

Filed Date 28-10-1994
National Phase Date 07-05-1996
Renewal Date 28-10-2001

Conventions

Number	Date	Country
93 MI A 2370	08-11-1993	Italy

Associations

No associations on record or public access is restricted

Actions

Date	Action
14-09-1998	Renew
15-04-1998	Registered
05-11-1997	Application Accepted
28-10-1994	Filed

Applicants & Licensees

Applicant: CRYOVAC, INC.
Address 100 Rogers Bridge Road, Duncan, South
Carolina 29334-0464, United States of America

Applicant & Licensee History

Applicant: W.R. GRACE & CO.-CONN
Address 100 Rogers Bridge Road, PO Box 464, Duncan,
South Carolina 29334, United States of America

Inventors

Buongiorno, Livio
Patrick, Ray E
Cerani, Luca
Ciocca, Paolo
Forloni, Roberto

Address for Service

No address for service on record or public access is restricted

Contact

A J PARK 6th Floor, Huddart Parker Building, 1 Post Office
Square, Wellington, New Zealand

Your Selection Criteria

IPONZ Database Search

IPOL Database Search

Collection:

Public

Patent Number:

276069

The information contained in the databases accessible through this site has been taken from files held at the Intellectual Property Office of New Zealand. This site is not intended to be a comprehensive or complete source of intellectual property information. The Intellectual Property Office will not be liable for the provision of any incorrect or incomplete information.

To obtain further assistance on the use of this Internet site please contact webmaster@companies.govt.nz or free-phone 0508 266726. Mobile and international callers telephone (03) 962 2602. To obtain information on how to apply for a patent, trade mark or design telephone (04) 560 1600.

Delivered: 04th October 2000 12:24:41